Structures of modulated crystals

Schutte, Willem Jan

Chapter 1

INTRODUCTION

This thesis presents experimental and theoretical studies concerning the structural aspects of modulated crystals in chalcogenides, bronzes and perovskites, containing transition metal elements. Both incommensurately and commensurately modulated crystal structures are considered.

1.1 General

Modulated crystals have received considerable attention in the last decennia, which is not only a consequence of the fact that these materials show incommensurability in the crystal structures, but also because they show a great variety of remarkable physical properties, as non-linear conductivity and high T_c superconductivity. Study of regularity of matter and its symmetry description has always been a subject in science and it still is. Until recently all crystals were described by three independent fundamental periodicities, as a result of a regular space filling of atoms. Crystals have translational and rotational symmetry elements, forming a three-dimensional space group symmetry, classified into a finite number of **230** possible space groups.

Incommensurate crystals do not fit in this classification. In a modulated crystal structure there is in addition to the three-dimensional symmetry some distortion, which is again periodic. In case this periodic distortion has a wavelength which is not a simple multiple of the basic periodicities, the structure is incommensurate. Otherwise the structure is commensurate, for which then a superstructure with a multiple unit cell dimension can be taken. Although the X-ray diffraction pattern of incommensurately modulated crystals has a very crystalline appearance with the typical sharp Bragg spots the diffraction pattern cannot be labelled by the three indices (h,k,l). Incommensurate crystals have one or more additional periodicities.

The symmetry of incommensurate crystals can be described by so-called superspace groups in which the additional periodicities are treated as a new coordinate in a higher $(3+d)$ dimensional space. In this so-called superspace the transla-

tional and point group symmetry is again present. In case of a one-dimensional modulation the X-ray diffraction pattern is described by four indices (h,k,l,m), expressing the components of a reciprocal wave vector in terms of four fundamental periodicities. The use of superspace groups to describe the symmetry of incommensurate crystals, can simply be extended to include commensurately modulated structures. The method of describing incommensurate structures is now well developed.

1.2 Scope

In this thesis structures of modulated crystals are determined by X-ray diiaction and the distortions have been analysed. The structural distortions of related compounds are compared. Several types of compounds are studied containing transition metal elements:

- Transition metal chalcogenides.
  An important condition for the modulation is that the transition metal elements can have various oxidation states with different metal configurations. Possible distortions are the formation of pairs, clusters or chains of metal and/or anion atoms. Two different types of these incommensurately modulated structures have been studied:

  - Charge density wave (CDW) structures.
    The modulations in these structures are connected with the electronic structure of these materials. However, in these compounds the large polarisability of the chalcogens is also important. Two different types of compounds in this category are studied. The first one shows clustering within a zig-zag chain of metal atoms, for Mo_2S_3 (Chapter 7), with a displacive modulation. The second exhibits a distortion towards pair formation of the anion chain, for $Au_{1-x}Ag_xTe_2$ (Chapter 5), with both displacive and substitutional modulations. The analogy between the two incommensurate distortion types in the structure of Mo_2S_3 and corresponding commensurate modulations in several transition metal chalcogenides is discussed (Chapter 8).
  - Order-disorder structures.
    Occupational modulations are observed in the close packed structure of metal-rich tellurides of nickel and copper in which partly occupied metal sites become ordered. An incommensurate phase exists with an ordering in one direction, which is accompanied by displacements of the atoms. This is observed for the compounds $Ni_{3\pm x}Te_2$ (Chapter 2) and $Cu_{3-x}Te_2$ (Chapter 3). The different behaviour of these compounds is ascribed to different interactions between the metal atom ordering and the tellurium lattice distortion. The order-disorder transitions to

the incommensurate and lock-in phases in $Ni_{3\pm x}Te_2$ and $Cu_{3-x}Te_2$ are analysed by applying Landau theory of second order phase transitions (Chapter 4).

- Mo-bronzes.
  In these CDW compounds there is a displacive modulation wave resulting in a very critical Mo-O overlap along the chain direction, observed for $K_{0.30}MoO_3$ and $Rb_{0.30}MoO_3$ (Chapter 6).

- Cu-perovskites.
  In the structure of these high T_c superconductors there is a combination of a displacive, substitutional and occupational modulation present. These effects are interpreted for the compound $YBa_2Cu_3O_{7-\delta}$ (Chapter 9).